NASA CR

RESEARCH ON A SUPERCONDUCTING NIOBIUM-THORIUM EUTECTIC ALLOY AND SUPERCONDUCTING COMPOSITES

by

H. E. Cline, B. P. Strauss, R. M. Rose, and J. Wulff

prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

CONTRACT NAS3-2590

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

RESEARCH ON A SUPERCONDUCTING NIOBIUM-THORIUM ALLOY AND SUPERCONDUCTING COMPOSITES

H. E. Cline, B. P. Strauss, R. M. Rose, and J. Wulff

Massachusetts Institute of Technology

ABSTRACT

Although detailed abstracts may be found in front of the sections of this report, we summarize here the year's research. In short, we have fabricated various composites in order to understand the behavior of the Nb-Th alloy. Three major results have come of this: a direct measurement of the proximity effect in a multiple structure, some predictions regarding the feasibility of Type II composites, and fabrication procedures which result in uniform deformation. The latter have been used to make preliminary Nb_3Sn composites of high promise, for flexible material of low cost and superior mechanical and superconducting properties.

INTRODUCTION

In NASA Report CR 54103 we described the formulation and fabrication of Nb-Th alloys of the autectic composition which have been reported to have very high critical fields(1). We also reported the results of electrical and magnetic measurements on the Nb-Th alloy. In general, reproducible results were not easy to obtain, and it became apparent that the alloy was more complicated than had been supposed, and also the theoretical interpretation which had been placed on the alloy's behavior(1) had been placed in doubt(2). The questions to be resolved were first, whether the eutectic lamellae could in fact give rise to the observed high-field behavior, or whether the latter were due to fine-scale precipitation or some other feature; and second, whether the supercurrent was carried by a combination of the discontinuous Nb-rich phase and portions of the Th matrix which had become superconducting through the coherency effect(3,4,5,6,7,8,9), or whether some continuity of superconducting material did in fact exist. In view of the difficulties experienced with the alloy itself, it was decided to fabricate a composite in order to achieve a predetermined "artifical" microstructure. A wire composite of Nb in a Cu matrix was then made up using the technique of Levi(10). Various special techniques were employed, and we recapitulate these in the first section for the convenience of the reader, although they may also be found in our previous report (NASA CR 54103). As we shall also recall in the second section, the critical field and overall level of the critical current density did not go up as the scale of the Nb-Cu composite was reduced, but instead decreased. The behavior was in sharp contrast to that of Bean(11) who investigated mercury-permeated Vycor, and indeed to our own results on the Nb-Th eutectic(1). In the latter case, our knowledge of the microstructure was not complete, and the nature of the material did not hold out any promise for further information of this sort. The structure of Bean's(11) material was well known, but involved a Type I superconductor.

Reference to the Ginzburg-Landau-Abrikosov-Gor'kov phenomenological theory(12-14) indicated that no enhancement of the critical field of a Type II superconductor should be expected until its size approaches the coherency distance, which in such cases is roughly an order of magnitude smaller than the penetration depth. In a composite, when such sizes are approached, coherency effects would be expected between superconductor and matrix(3-9) which would, in our case, lower the energy gap for superconductivity in the niobium filaments considerably. The second section of this report describes the superconducting measurements on the composite of T_c, $H_c(T)$, and $J_c(H)$.

In the third section, we discuss the results, of which two are of major interest. First, coherency has been observed at sizes as large as 4000 Å in our composites which confirms work previously done on evaporated and electrodeposited films(3-9), and contradicts the doubts previously expressed(2) regarding the coherency effect. Second, the composite has apparently been deformed uniformly by our technique down to 100 Å filament sizes, a surprising result. Further to exploit the uniformity of the drawing technique, we proceeded to make up simple Nb-Sn composites, the advantage of which is that a thin layer of reacted Nb_3Sn could be made inside, rather than outside the wire as is common in most of the commercially developed products. The potential of such a composite is that the Nb-Sn wire could easily be rolled to ribbon before reaction at 900-1000°C, and the resulting Nb_3Sn layer would form at the neutral axis of the ribbon, a much sounder and safer place for a brittle phase (such as Nb_3Sn) than the outside of the ribbon.

The fifth section of this report describes the composite of Nb and Sn which was successfully fabricated and reacted after a few false starts. High field measurements were made of the critical current density as a function of the applied field, which are reported in the sixth section.

Finally, the sixth section contains a discussion and recommendations for future work.

REFERENCES

1. H. E. Cline, R. M. Rose, and J. Wulff, J. App. Phys., 34, 1771 (1963).
2. A. B. Pippard, Rev. of Mod. Phys., 36, 328 (1964).
3. P. Hilsch and R. Hilsch, Naturwissenschaten, 48, 549(1961).
4. P. Hilsch and R. Hilsch, Z. Physik, 180, 10 (1964).
5. P. Hilsch, R. Hilsch, and G. von Minnigrode, Proc. VIIIth International Conference on Low Temperature Phys., p. 381, Butterworth's, Washington (1963).
6. P. H. Smith, S. Shapiro, J. L. Miles, and J. Nicol, Phys. Rev. Letters, 6, 686 (1961).
7. R. H. Parmenter, Phys. Rev., 118, 1173 (1960).
8. L. N. Cooper, Phys. Rev. Letters, 6, 689 (1961).
9. A. C. Rose-Innes and B. Serin, Phys. Rev. Letters, 7, 278 (1961).
10. F. P. Levi, J. App. Phys., 31, 1469 (1960).
11. C. P. Bean, M. V. Doyle, and A. C. Pincas, Phys. Rev. Letters, 9, 93 (1962).
12. V. L. Ginzburg and L. D. Landau, JETP (USSR), 20, 1064 (1950).
13. A. A. Abrikosov, JETP (USSR), 32, 1442 (1957). Translation: Soviet Physics, JETP, 5, 1174 (1957).
14. L. P. Gor'kov, JETP (USSR), 36, 1918 (1959). Translation: Soviet Physics, JETP, 9, 1364 (1959).

I. THE Nb-Cu COMPOSITE

ABSTRACT

This section describes the successful fabrication by mechanical deformation of a composite consisting of continuous columbium wires in a copper matrix, where relatively uniform, consistent wire sizes down to a few hundred Angstroms or less appear to have been achieved while retaining continuity of the wires. The method of fabrication was that of Levi(1).

The composite of fine niobium wires in copper was chosen to investigate the size and proximity effects of a superconductor in a normal matrix. These materials also had desirable mechanical and chemical properties. The fabrication technique was developed from the method of Levi(1).

FABRICATION

The starting materials were 1/8" diameter electron-beam melted Nb rod, and OHFC copper tubing with 0.375" o.d. and 0.032" wall thickness. The tubing was swaged onto the rod and the ensemble then drawn to 0.0345" diameter wire which was cut into 56 pieces. These pieces were fitted into another piece of copper tube, and the ensemble drawn down again to 0.0345" diameter. This procedure was repeated four times, and on the final sequence, the wire was drawn down to 0.006" diameter, which, on the assumption of uniform straining of the Nb and Cu, corresponds to a Nb diameter of about 100 Angstroms. Before assembling each composite prior to a drawing sequence, the surfaces of the wires and tube were carefully cleaned, degreased with a solvent (trichloroethylene) and abraded with No. 600 metallographic paper and recleaned. Drawing was done at the uniform rate of one inch per minute by mounting dies and wire in an Instrom tensile testing machine. Commercial wire-drawing equipment was found to be insufficiently even in its drawing rate, and all attempts to make composites using commercial equipment in our laboratory failed. The low drawing rate was also necessary. The lubricant used was of the MoS_2 type. Surface preparation of the wires was not necessary.

At various stages in the fabrication, specimens were secured for optical electron micrography and diffraction. For the second and third sequences, optical metallography with routine diamond-dust polishing and no etching sufficed to delineate the structure. For subsequent operations, electron micrography was necessary. The Cu matrix was removed by etching with 50% HNO_3, the resulting columbium "wool" was washed, broken up by ultrasonic cavitation, and fished out of the water with a standard grid used for transmission electron micrography.

Figure 1 shows a transverse section of the composite during the second repetition of the drawing sequence, where the Nb filaments are now somewhat below 0.001" in diameter. Separations are readily visible between the copper "colonies" which we believe have been caused by the polishing procedure. The "colonies" could be manually separated if the outer copper was removed; thus, cold welding did not occur at this stage. Figures 2 and 3 show transverse and longitudinal sections during the third drawing sequence, with a Nb wire size of about 2 microns. We believe the discontinuity shown in the longitudinal sections to be only apparent, resulting from the shifting of the wires from the plane of the section. We managed to separate wires about 6" long and 2 microns in diameter from the Nb "wool" which remained after the Cu was etched away prior to the electron micrography. (Small solder weights suspended by these wires did not lead to fracture until streeses of the order of 2×10^6psi were attained.)

Figure 4 shows a series of electron micrographs of the niobium "wool" which was released from the copper matrix by etching, at various stages of the final reduction. Some residue was left by the etching, as can be seen in the upper two micrographs, of the larger material, i.e., 200-800 Å. The residue, or unetched copper, has apparently bonded the Nb fibers in the lower two micrographs together. Electron diffraction pictures showed the spots for Nb, plus circles for another substance which we have not identified, but which presumably is the residue. Indirect evidence for the continuity and integrity of the structure has been obtained in the form of superconductivity measurements(2). The composite appears to have been deformed uniformly, with Nb and Cu reducing equal amounts, down to the 0.006" outer composite diameter, which corresponds to a 100 Å Cb filament size, with about 10^7 filaments in the wire cross-section. X-ray diffraction revealed no change in the lattice parameter for specimens down to 600 Å. Insufficient material was available from finer specimens for X-ray measurements.

REFERENCES

L. F. P. Levi, *J. App. Phys.*, *31*, 1469 (1960).

2. H. E. Cline, B. P. Strauss, R. M. Rose, and J. Wulff, "Superconductivity of a Composite of Fine Niobium Wires in Copper", to be published.

Figure 1: Transverse section of the composite during the second drawing repetition. Final polish 1/4 micron diamond dust. No etch.

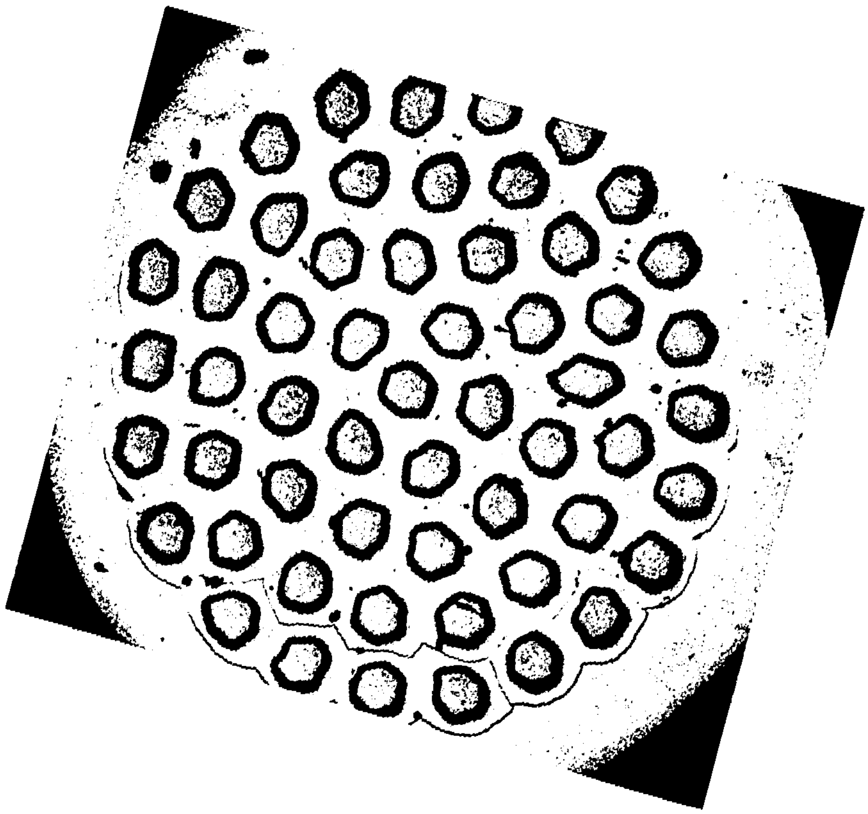


Figure 2: Transverse and longitudinal section of the composite during the third draw. Final polish 1/4 micron diamond dust. No etch.

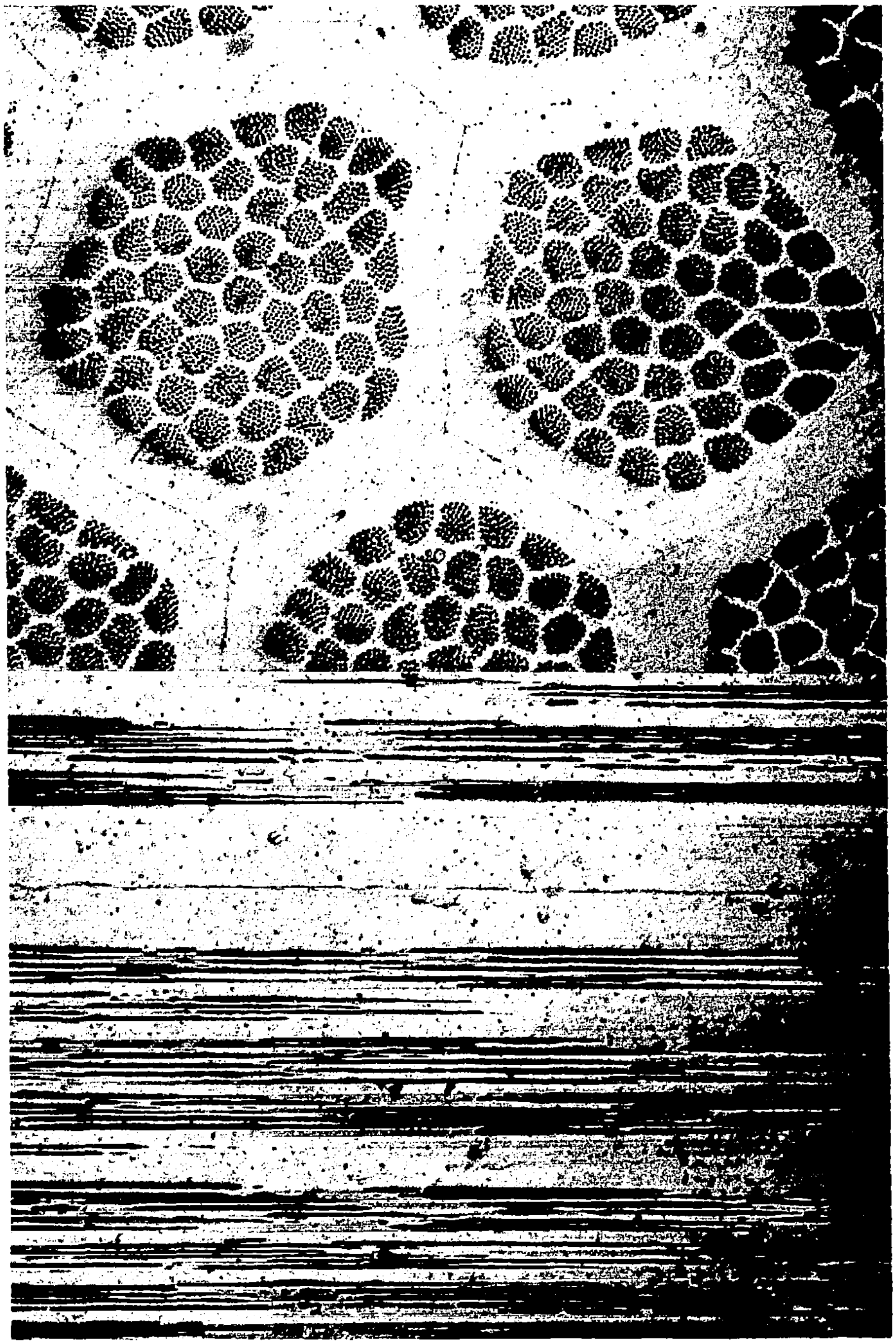


**Fig. Nb-Cu Trans. and Long.
150X**

Figure 3: Same as Figure 2, higher magnification.

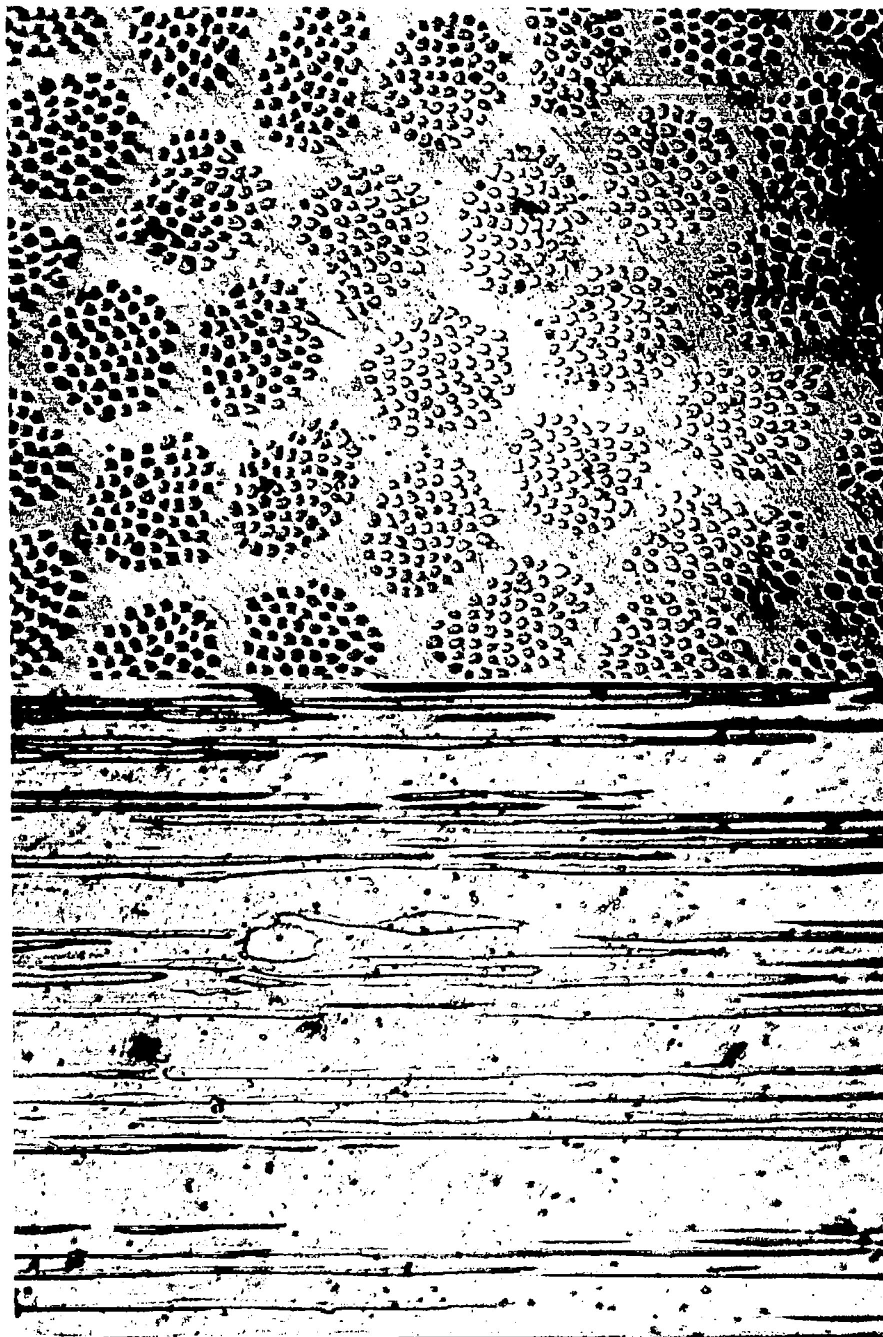


Fig.   Nb–Cu Trans. and Long.
          500X

Figure 4: Electron micrographs of Cb filaments extracted by etching from the finest specimens.

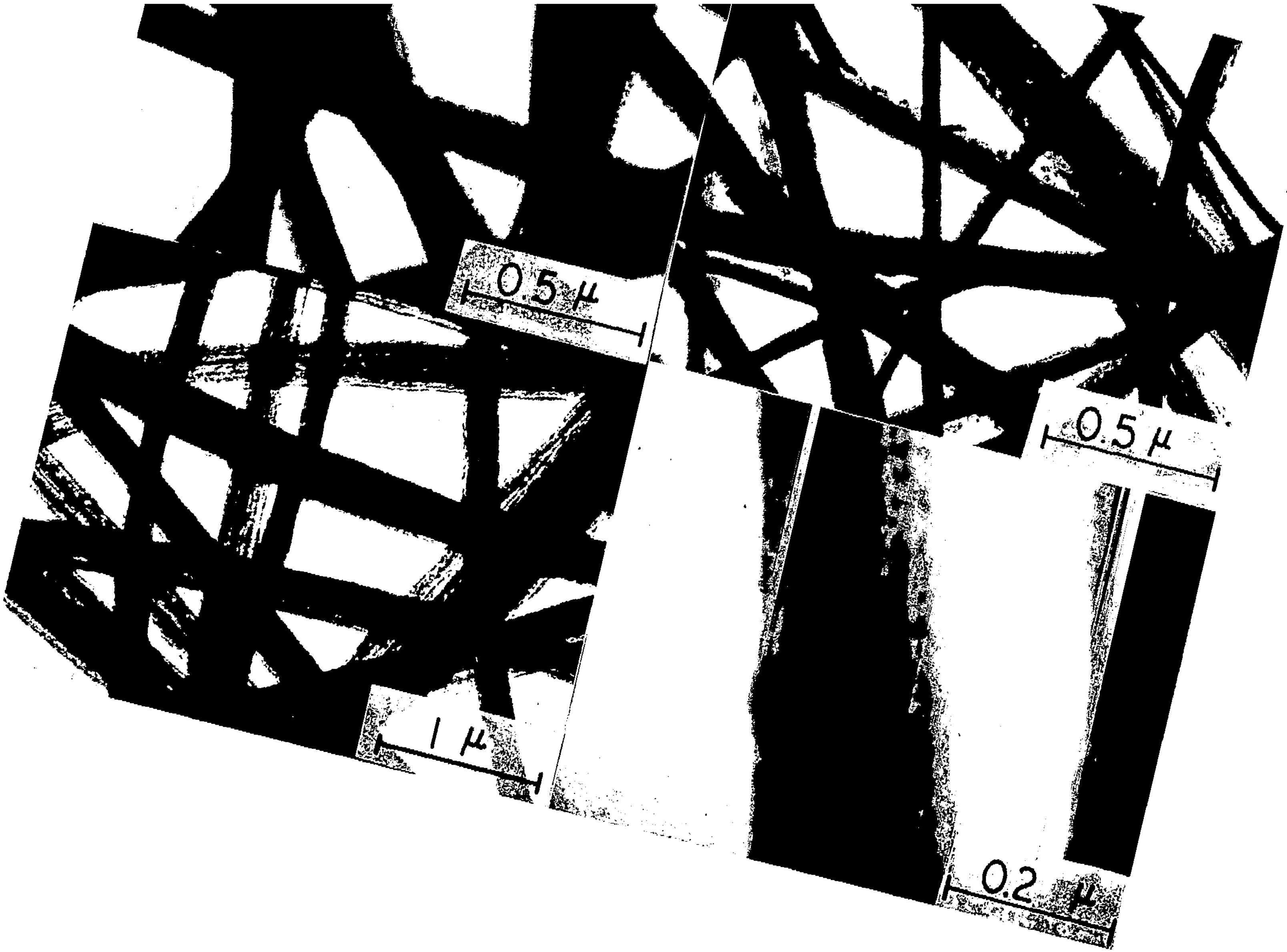
(a) outside composite diameter 0.0455"

(b) outside composite diameter 0.0197"

(c) outside composite diameter 0.0061"

(d) outside composite diameter 0.0061"

In (c) and (d), please note that each dark "strand" apparently consists of a bunch of Cb filaments glued together by some unidentified substance. The Cb filament diameter appears to be in the vicinity of 100 Å.


0.5 μ
1 μ
0.5 μ
0.2 μ

II. SUPERCONDUCTIVITY OF THE Nb-Cu COMPOSITE

ABSTRACT

The following superconducting properties of the Nb-Cu composite were measured: the critical temperature, critical transverse magnetic field as a function of temperature, and critical current density at 4.2°K as a function of transverse magnetic field. As the diameters decreased, T_c, $H_c(T)$, and J_c all decreased. The results are discussed in the next section.

INTRODUCTION

To investigate the size effect and the proximity effect in the composite, the critical temperature, critical field as a function of temperature, and critical current density as a function of applied transverse field at 4.2°K were measured. Bean(1) observed the size effect in a synthetic material consisting of fine filaments of mercury in a vycor glass matrix. The critical field of this material was increased because of the small size of the mercury filaments compared to the penetration depth λ. The glass matrix did not change the critical temperature of the mercury.

On the other hand, a metal matrix is expected to lower the transition temperature because of the proximity effect. In experiments involving metallic films deposited by electroplating (2-6) and evaporation and deposition in vacuum(7,8-10), changes in transition temperature have occurred. Diffusion and the formation of intermetallic compounds can play a critical role on experiments on the superconductivity of superimposed metals(11-13). However, experiments which show a proximity effect have been done in systems of limited solubility(7) and on samples prepared below 10°K where diffusion is negligible(9). This proximity effect depends on the thickness of the films, the type of metals used, and their residual resistivities(9).

Specimens and Measurements

Samples of wire were chosen at various sizes, at various stages in the fabrication procedure. The critical current density at 4.2°K as a function of transverse applied magnetic field was determined by the four-point resistive technique. Voltage leads were soldered and current leads pressed directly onto the composite. A criterion of one microvolt across a 2.5 cm section of wire was used for the transition.

The critical temperature and the transverse critical field as a function of temperature were measured by a resistive technique with a search current density of 50 amps/cm^2. For the critical temperature, the voltage across the specimen was monitored as a function of temperature. The specimen was in thermal equilibrium with a copper block which was immersed in vapor over a liquid He bath. The temperature was measured with a calibrated germanium resistance thermometer. For the critical field, the magnetic field was increased at constant temperature, and the point at which half the normal resistance returned was taken as the critical field. Temperatures below 4.2°K were attained by reducing the pressure over the liquid helium bath. Figures 1 and 2 show the layout of apparatus for the measurement of $H_c(T)$. The apparatus for T_c is similar.

RESULTS

The transition temperatures were markedly depressed as the niobium filament size was decreased. Figure 3 shows the complete resistive transitions of four of the composites, and bulk niobium, i.e., wire 0.025 cm in diameter. The transitions are increasingly broad as the filament size decreases. Figure 4 plots the transition temperature of seven of the composites and the Nb wire, as a function of Nb filament size. We have taken as T_c the temperature at which the specimen has half its resistance for the normal state. Figure 5 shows the resistive transverse critical field as a function of temperature, with the half-point of the resistivity again used as the transition field criterion. The critical field appears to be even more sensitive than T_c to the size. Figure 6 presents critical current density at 4.2°K as a function of transverse applied field, which was presented in our previous report. Here, a transition criterion of one microvolt across a gauge length of 2.5 cm was used.

The value of J_c decreases as the size decreases for a given value of the applied field. The slopes of the curves in Figures 5 and 6 also appear to fall off as the size decreases. In connection with Figure 6, we should point out that the current density is calculated on the basis of the total composite area, of which approximately 6% is Nb. Consequently, if the supercurrent is assumed to be concentrated in the Nb, the critical current density of the Nb is about 17 times the J_c in Figure 6.

Figure 1: Layout of cryogenic apparatus.

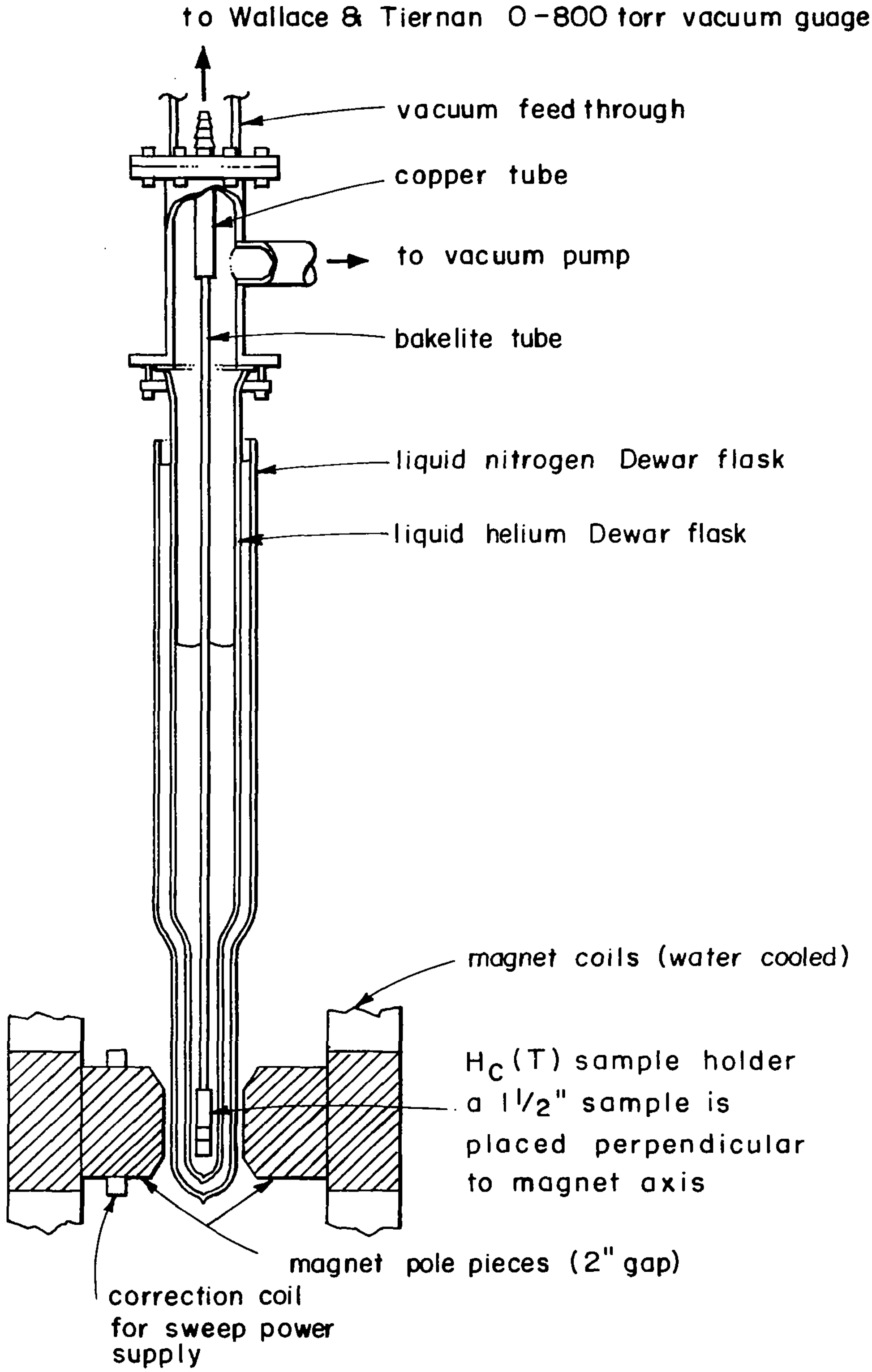
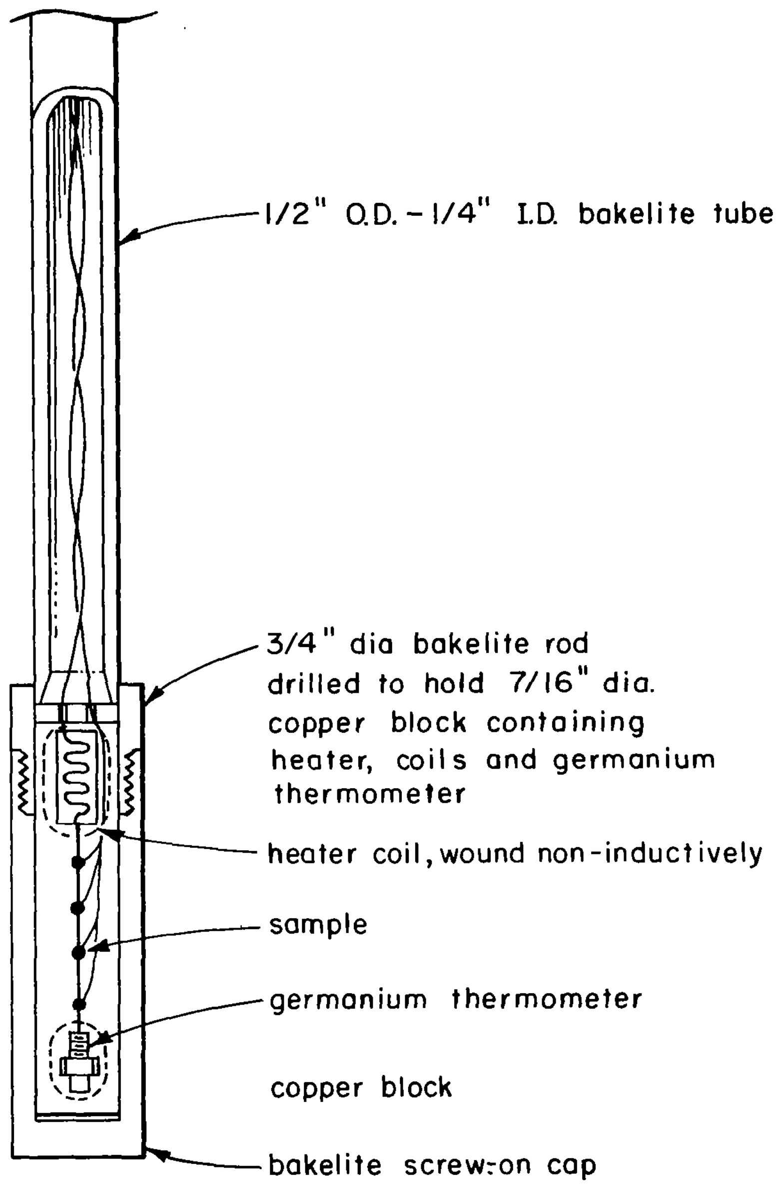

to Wallace & Tiernan 0-800 torr vacuum guage
vacuum feed through
copper tube
to vacuum pump
bakelite tube
liquid nitrogen Dewar flask
liquid helium Dewar flask
magnet coils (water cooled)
$H_C(T)$ sample holder
a 1½" sample is
placed perpendicular
to magnet axis
magnet pole pieces (2" gap)
correction coil
for sweep power
supply

Figure 2: Detail of sample holder for H_c vs. T meas



1/2" O.D. - 1/4" I.D. bakelite tube
3/4" dia bakelite rod drilled to hold 7/16" dia. copper block containing heater, coils and germanium thermometer
heater coil, wound non-inductively
sample
germanium thermometer
copper block
bakelite screw-on cap

Figure 3: Resistive transitions of four composites and Nb wire. ($J = 50$ amps/cm^2).

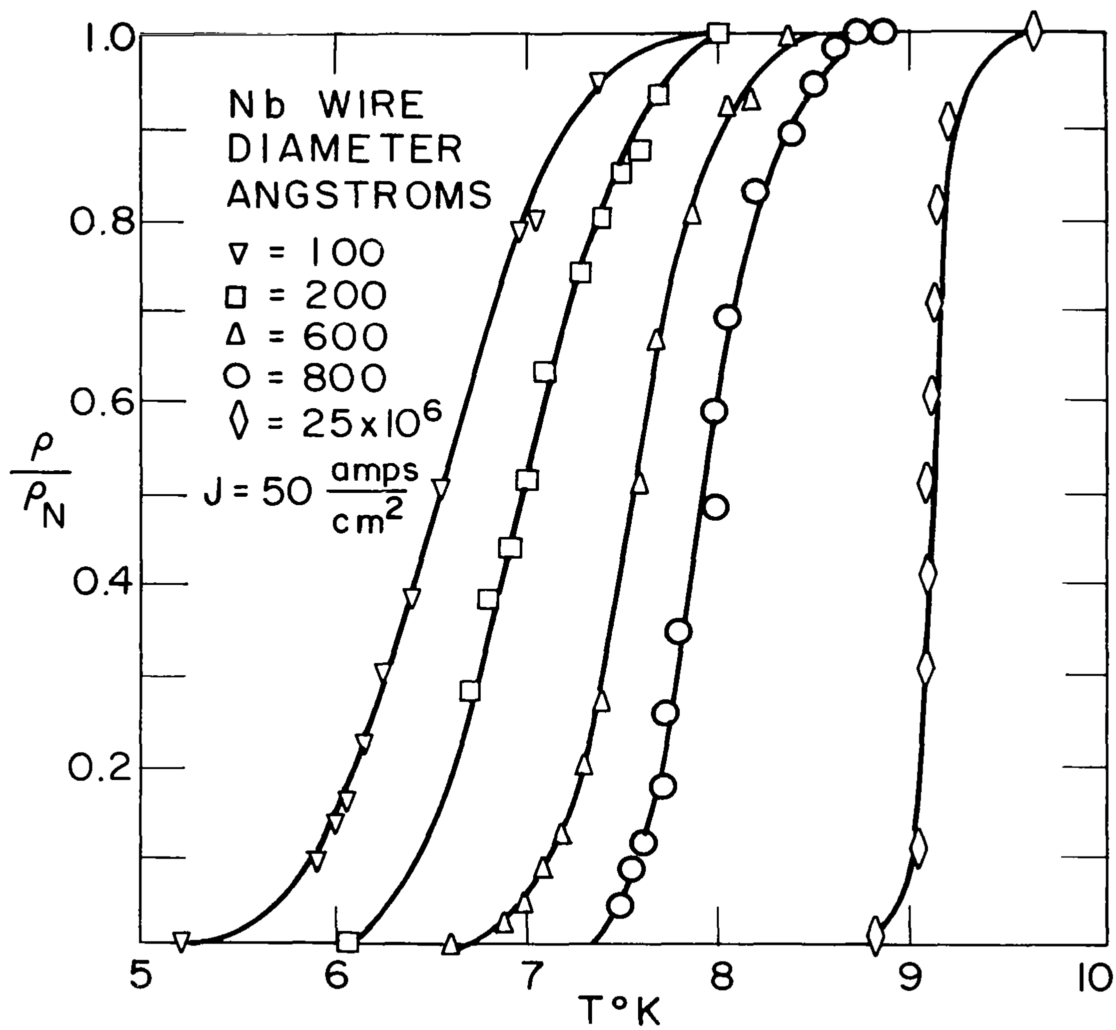
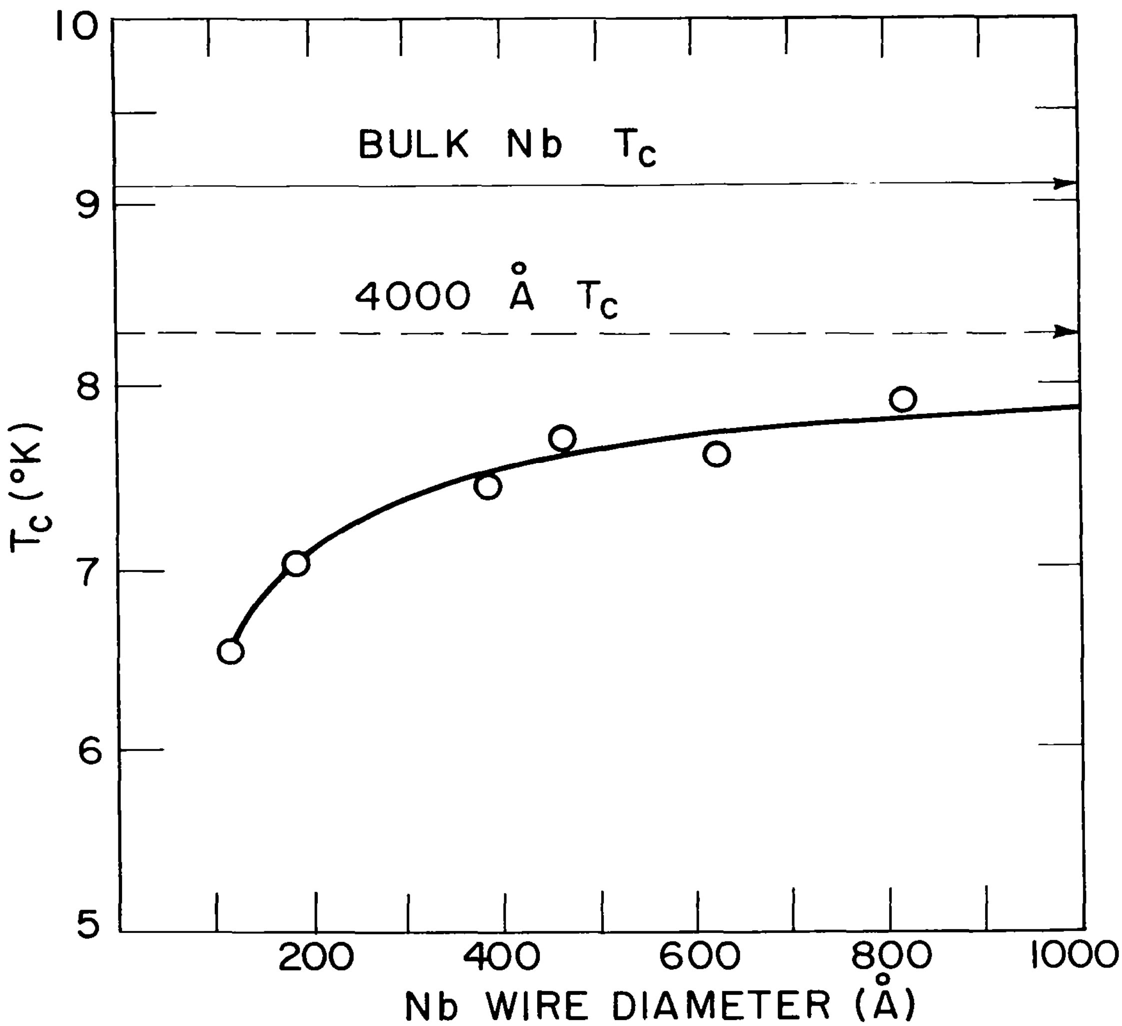

Nb WIRE
DIAMETER
ANGSTROMS
∇ = 100
□ = 200
Δ = 600
O = 800
◊ = 25x10^6
J = 50 amps/cm^2
1.0
0.8
0.6
0.4
0.2
ρ/ρN
5
6
7
8
9
10
T°K

Figure 4: Transition temperature as a function of filament size. The Temperature at which half the normal resistivity of the composite is restored is taken as T_c. (Same search current as in Figure 3.)



BULK Nb T_c
4000 Å T_c
T_c (°K)
10
9
8
7
6
5
200
400
600
800
1000
Nb WIRE DIAMETER (Å)

Figure 5: Resistive transverse critical field as a function of temperature for the four composites shown in Figure 3. One half the normal resistivity is again used as the criterion. (Same search current as in Figure 3.)

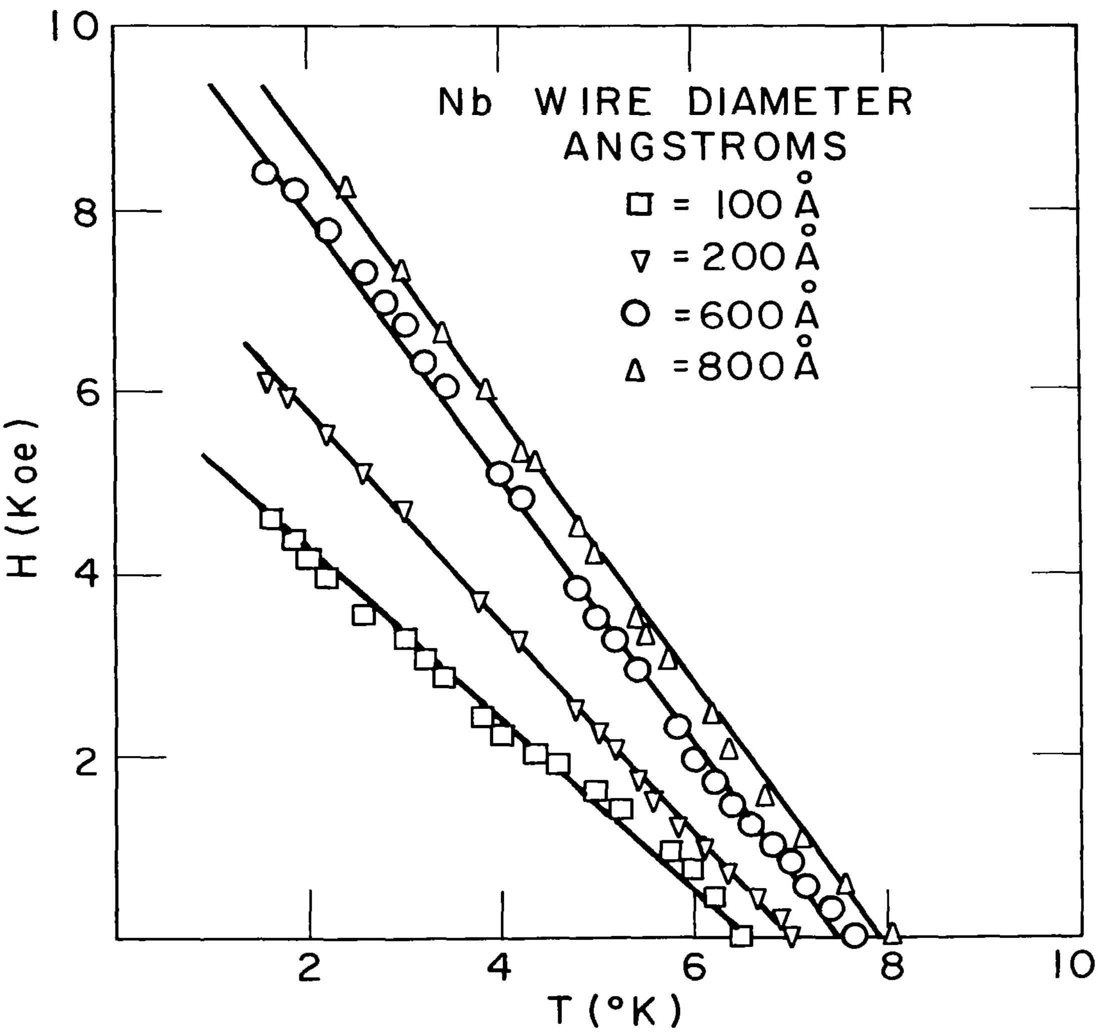
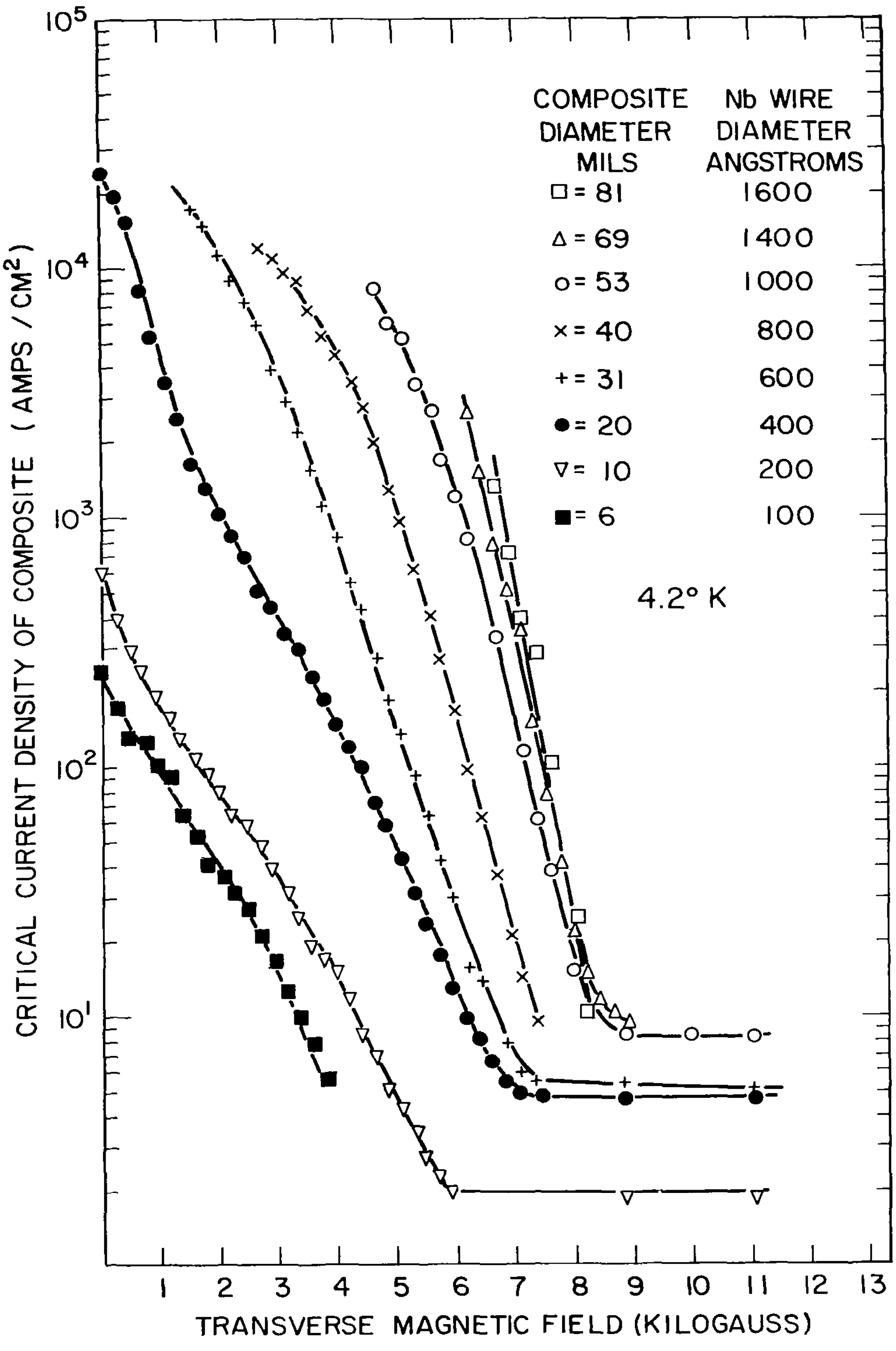

Nb WIRE DIAMETER
ANGSTROMS
□ = 100 Å
▽ = 200 Å
○ = 600 Å
△ = 800 Å
H (Koe)
T (°K)
10
8
6
4
2
2
4
6
8
10

Figure 6: Critical current density at 4.2°K as a function of the transverse applied magnetic field.



CRITICAL CURRENT DENSITY OF 9.8×10^6 NIOBIUM WIRES IN A COPPER MATRIX

III. DISCUSSION: THE Nb-Cu COMPOSITE

ABSTRACT

The superconducting behavior of the composite, that is, the depression of $J_c(H)$, $H_c(T)$, and T_c as the size was decreased can be accounted for by a lowering of the energy gap in the Nb by the proximity effect. The results are very close to those observed on superimposed thin films. It is therefore not expected that high critical fields can be attained by composites involving a Type II superconductor in a matrix of a nonsuperconductor.

The accomplishment of uniform deformation down to 100 Å filament size in these composites is notable, and there is no reason to expect this combination to be the only one in which such reductions are possible.

The critical field of the composite was not increased significantly with decreasing size for any composite between 10^6 and Å. Considering that Nb is a Type II superconductor, no increase is anticipated until the diameters of the Nb filaments approach the order of the coherancy distance in the case where vacuum surrounds the filaments.

Abrikosov has solved the size effect problem for Type II thin films in vacuum(1). The presence of the copper must modify the boundary conditions and such modifications should account for the results observed in this investigation, for the depression of $H_c(T)$, T_c, and J_c.

The critical temperature was decreased in a manner very similar to the results of Hilsch et al.(2-4) for superimposed thin films, although the nature of the specimens was quite different. In the case of Hilsch et al., diffusion, contamination, and compound formation was eliminated by very low temperatures for deposition, very high vacua, and careful attention to the solid solubilities of the films. We believe that many of these factors are inherent in the composite as well. All fabrication was performed at room temperature, where interdiffusion of Nb and Cu should be very small. No intermetallic compounds have been reported for the Nb-Cu system. No contamination is anticipated as a result of the fabrication, as the Nb is enclosed completely by a continuous copper envelope, and ever exposed. The Nb-Cu interface is probably a very "clean" one, possibly atomically clean. For example, consider the initial impurity layer on the starting Nb (.32 cm diameter) to be 100 Å thick. If the layer is assumed to strain uniformly with the composite, the impurity layer would be monomolecular when the Nb filament size is below about 5×10^{-3}cm, and much less dense at the sizes used in much of this work.

Further evidence of the lack of contamination is found in the X-ray lattice parameter measurements.

Strain effects on the superconductivity are expected to be small, as both materials have cubic lattices of high symmetry. In addition, the similarity of the geometry precludes any size dependence of induced strains. which means that a strain induced shift in the superconducting properties if it exists, should be the same for all samples.

The Nb filaments are apparently unbroken and not in contact with each other. The electron micrography indicated continuous filaments and handling of the Nb after matrix removal confirmed this observation. The Nb filaments formed a woolly mass from which individual filaments of a micron diameter as long as 15 cm could be separated. The uniform reduction of the Nb is further evidence for continuity, as is the high J_c of the composite shown in Figure 6. The separation of the filaments is suggested by both the microstructure and the lack of trapped flux in the magnetization of the composite, reported last year.

It is significant that such fine sizes are achievable by mechanical deformation, and that the matrix may be so simply removed. We feel that critical field enhancement in a fine composite of a Type II superconductor in a matrix of non-superconductor will not occur, as the proximity effect will dominate long before the composite is sufficiently fine. Where the matrix is a superconductor, as in the case of Nb-Th(5), the situation is different.

REFERENCES

1. A. A. Abrikosov, Soviet Physics, JETP, 20, 480 (1965).
2. P. Hilsch and R. Hilsch, Naturwissenschaften, 48, 549 (1961).
3. P. Hilsch and R. Hilsch, Z. Physik, 180, 10 (1964).
4. P. Hilsch, R. Hilsch, and G. von Minnegrode, Proc. VIIIth International Conference on Low Temperature Physics, p. 381, Butterworth's Washington (1963).
5. H. E. Cline, R. M. Rose, and J. Wulff, J. App. Phys., 34, 71(1963).

IV. OTHER COMPOSITES, LESS SUCCESSFUL

ABSTRACT

Other composites were also attempted. The "inverse" Nb-Cu composite, i.e., Cu wires in an Nb matrix was fabricated with both thick and thin walls. The magnetization curves for these composites showed evidence of a high degree of flux jumping and violent current quenching. Nb in a Nb-40% Ti matrix was also fabricated with no significant improvement.

Two composites of niobium-clad copper were produced to test the superconducting properties of a honey-comb structure of thin niobium. Niobium tubing, 1/4" O.D.(.020" wall) was swaged onto a .2" O.F.H.C. copper rod. The niobium-clad rod was drawn to .0345", cut into 56 pieces, and bundled into O.F.H.C. copper tubing 3/8" O.D.(.032" wall). This composite will be referred to as the "thin-walled" composite. The other, the "thick-walled" composite, was made by drilling a 1/4" hole in a 1/2" Nb rod. A copper 1/4" rod was placed in the niobium tube and swaged in place. Because of the brittleness observed in the thin-walled composite, solid rod was bored out to give a tube of higher purity and less strain than commercial tubing. Figure 1 shows a comparison of the thin-walled and thick-walled composites on the first series of drawing passes. This material was drawn to .0345", cut in 56 pieces, and bundled into a copper tube. The copper jacket of the thick-walled composite was not strong enough to pull the composite through the dies. This caused a loss of most of the material due to breaking of the points in drawing. After drawing to .0345", the copper jacket was removed in 50% HNO_3. The niobium-clad copper wires stuck together by cold welding. Seven bundles of wires were rebundled and drawn down to 0.100" where the material broke up.

The thin-walled composite met with more success. Figure 2 shows the thin-walled composite together with its inverse during the second draw. Figure 3 shows the same at a higher magnification, etched and unetched. The top portion of Figure 4 shows a closer view with heavier etching. After this draw, this composite, too, failed. Finally, the bottom of Figure 4 shows a Nb in Nb-40% Ti composite which did not survive the second draw either.

At this point, we can set up some general requirements for success with this method of making composites. There are four problems:

Problem 1 - Rippling

Rippling of the interface has occurred to some degree in all the composites. Rippling is most pronounced when the tube wall is thick and the inner material is softer than the outer material. Rippling is always observed on the inner surface of a drawn empty tube. In swaging, the rippling is very pronounced and, combined with twisting of the tube, may cause the inner material to break up. In uniform deformation, rippling should not occur.

We believe that rippling is caused by the instability in shrinking the inner radius proportionally more than the outer radius. In uniform deformation, the inner and outer radii reduce in the same proportion; but an empty tube or a tube filled with a soft material becomes non-uniformly deformed and there is a tendency for the wall to thicken. The solution to this problem is to match the mechanical properties, namely, yield strength of the constituents or to make sure the inner material is harder than the outer material. A high work hardening would help combat this instability.

Problem 2 - Shearing of Outer Jacket

If the outer jacket is soft or thin, or if there is no bond between the jacket and material, there may be a shearing of the outer jacket. In the case of no bond between the jacket and material, the jacket must be strong enough to pull the material through the die. If not, the jacket will simply break in tension. However, if there is a bond between the jacket and material, whether it is just compression, friction, cold welding, or a chemical bond, it helps transmit the drawing stress to the inner material through a shear stress, and allows one to use a weaker jacket, as the jacket has only part of the drawing stress. But right at the grips, the jacket may shear off and make drawing difficult, if not impossible.

Problem 3 - Extrusion of Softer Material at Ends

This problem is encountered when short lengths of material are drawn with a soft inside as we often did with experimental materials. The solution is simply to use long lengths where end effects are negligible.

Problem 4 - Breaking

This is the most serious problem as it severely limits composites to very ductile materials. Even using ductile materials may not stop breaking, as the many wires present in a composite increase the chance of a fracture. If the fracture of one wire causes other wires to break, then the composite has little chance of success. The propagation of fracture can be arrested by a soft ductile phase, as in the copper-clad niobium. Annealing may help make a composite ductile or high temperature treatment may be used to bond the material together. The composites made thus far are not useful D. C. magnet materials. Rather, their significance lies in obtaining a better understanding of how to make and how not to make mechanical composites.

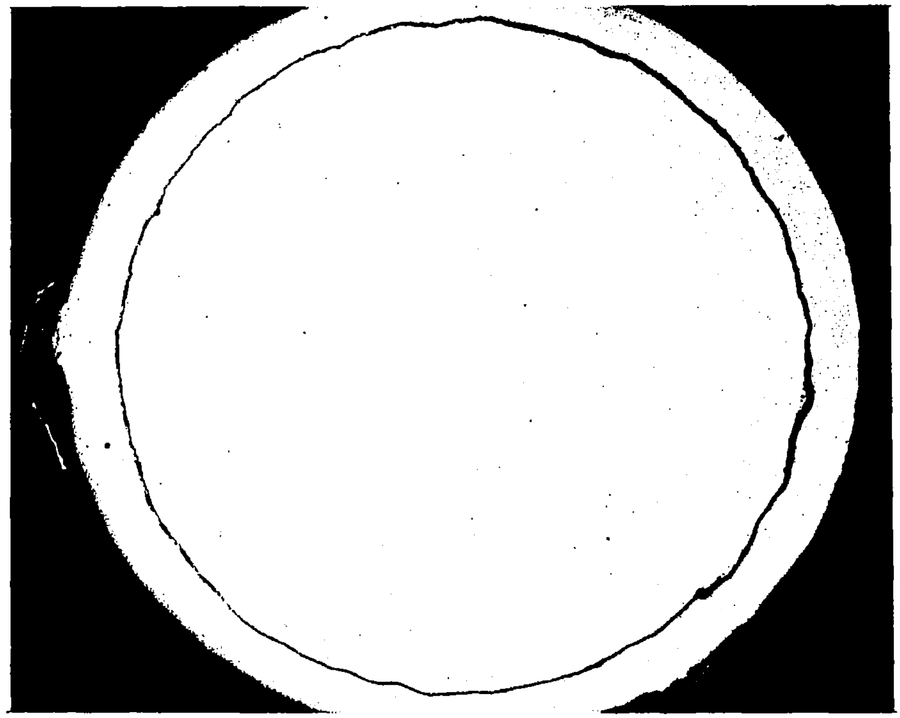
Even when the four problems are not dealt with, some success at the first and second draws should be possible. One obvious application is the fabrication of Nb_3Sn wire. Ultimately, we would like an array of Nb_3Sn wires in a Nb matrix. If the wires are fine enough, the material may bend elastically, like the behavior of fibre-glass. Even on the first draw, wire or ribbon could be produced and reacted. The Nb_3Sn would be at or near the center of the wire or ribbon, mechanically a very desirable place for it.

SUPERCONDUCTING TESTS ON THE Nb-Cu "INVERSE" COMPOSITE

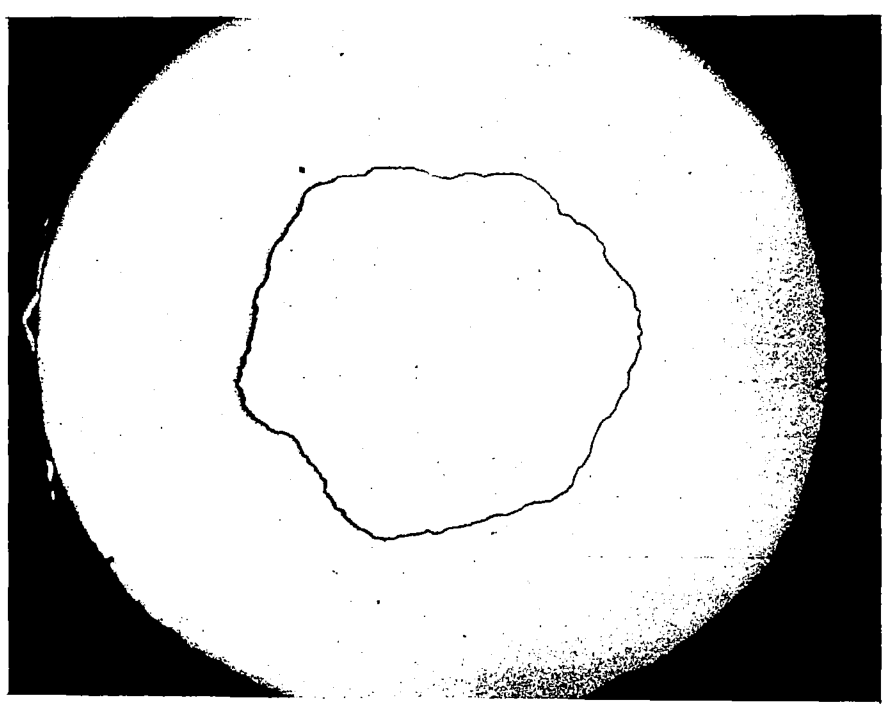
Magnetization measurements were made on 1/8" samples 1/2" long. The thick-walled and thin-walled material after the first draw gave the typical irreversible magnetization curve for worked Nb. The field at which the magnetization went to zero was 6 kilogauss for the thin-walled material, and 5 kilogauss for the thick-walled material, showing that the thin-walled material has more cold work or is impure. After the first bundling, the thick tube composite showed a peculiarly shaped curve with two peaks and a negative trapped flux. This result is actually due to apparatus error due to a very severe flux jump which overloaded all the D.C. amplifiers and shifted the zero point of the integrator.

J_c vs. H measurements were made on the material. Because of the high critical current density, we could not measure wire above .012". Even these thin wires burned out due to current quenches. However, enough data were taken to show that this material did not act significantly different from niobium. It is significant that both severe current quenches and severe flux jumping occur in the same material. By comparison, the original Nb-Cu composite had very "soft" quenches.

Figure 1: The two Nb-Cu inverse composites during the first draw.

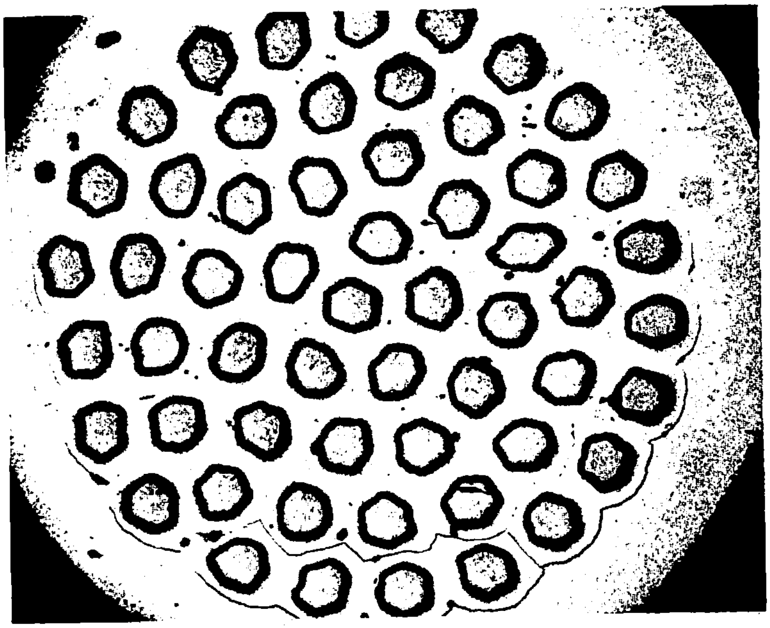


Copper in thin-walled niobium tube.
(unetched) O.D. is .125 inches.

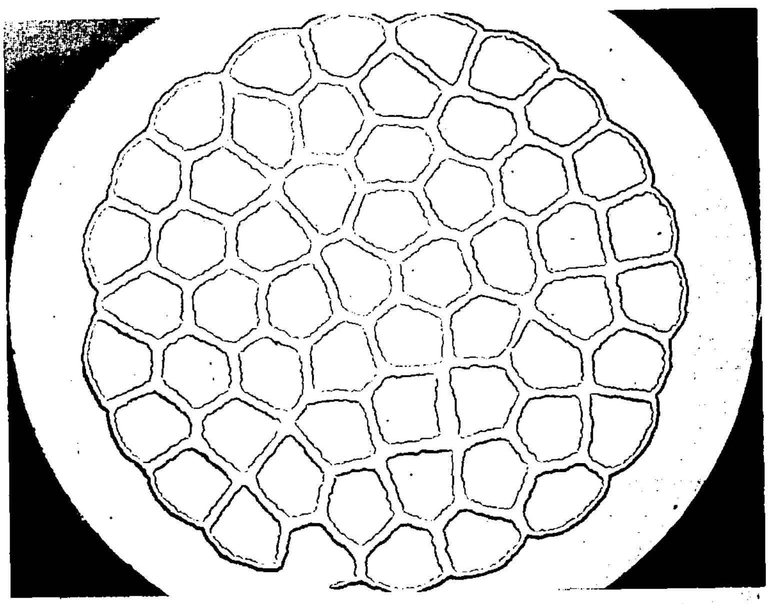


Copper in thick-walled niobium tube.
(unetched) O.D. is .125 inches.

Figure 2: The thin-walled inverse composite during the second draw compared to the original Nb-Cu composite at the same stage.

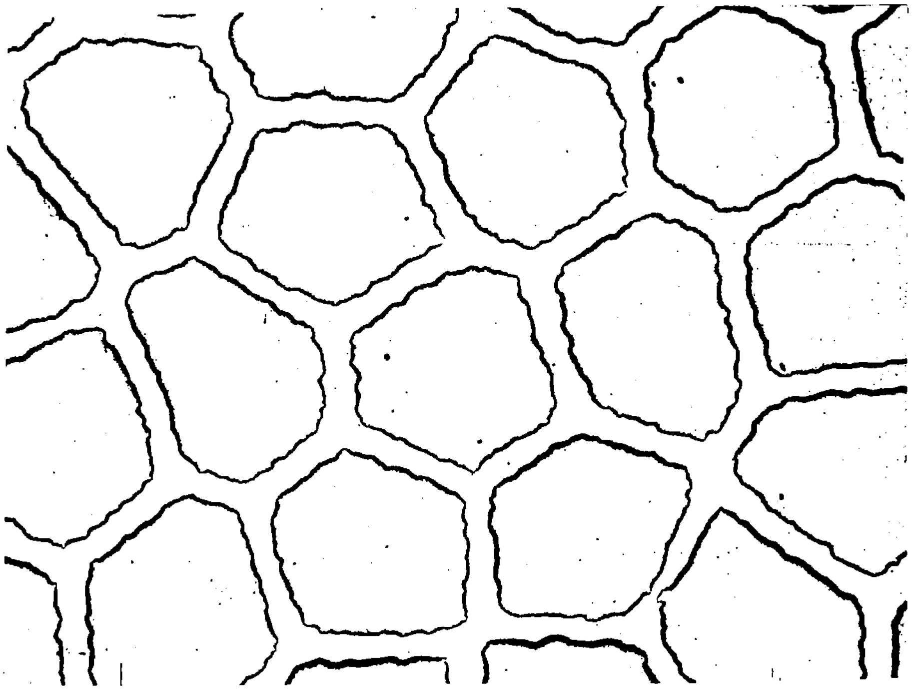


Niobium in copper matrix (unetched).
O.D. is .125 inches.

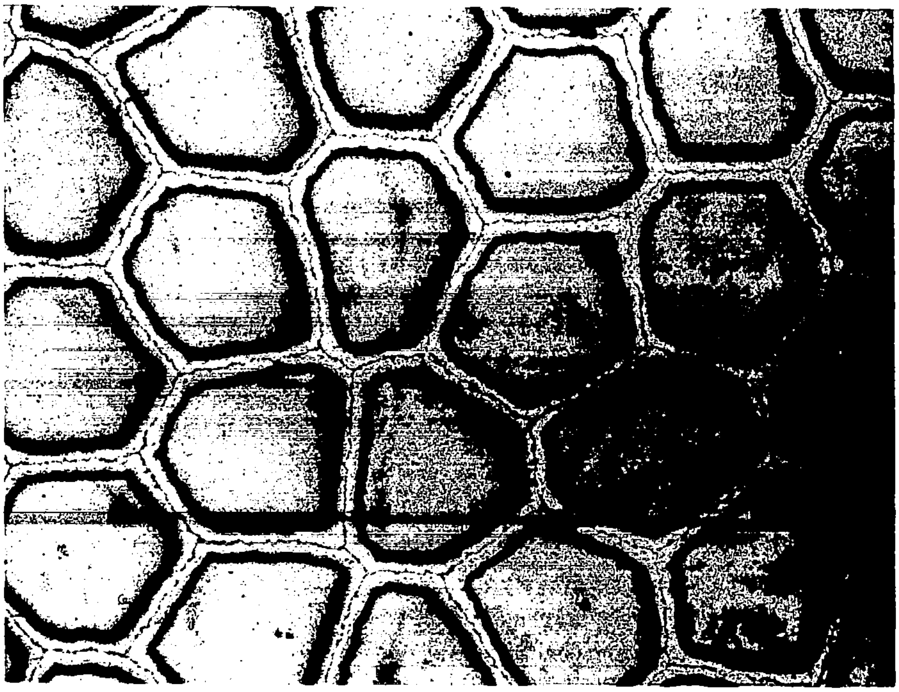


Copper in thin-walled niobium matrix.
(unetched) O.D. is .125 inches.

Figure 3: The thin-walled composite, etched and unetched.

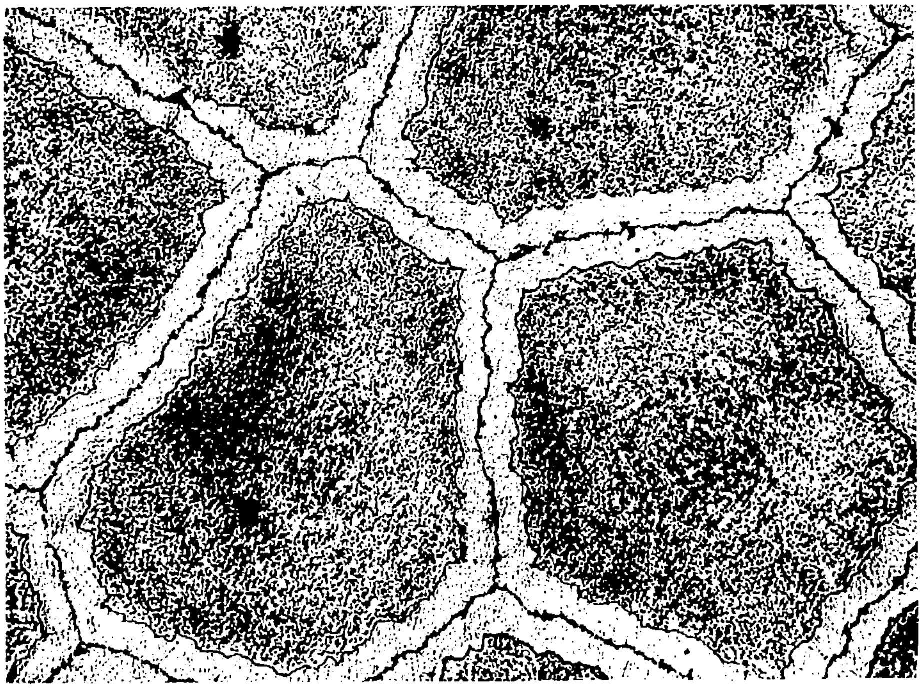


Copper in thin-walled niobium matrix.
(unetched) 50X.



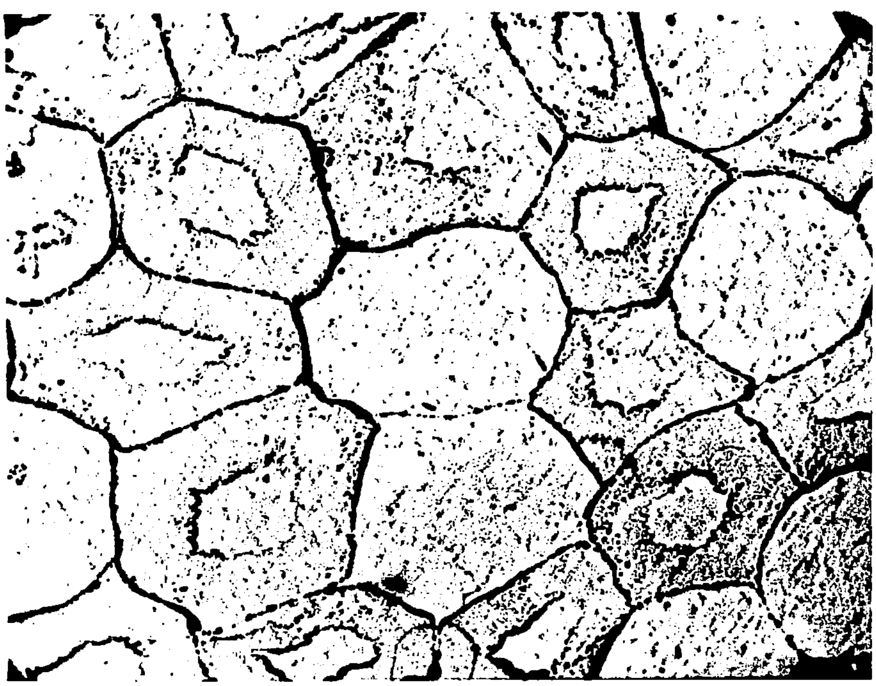
Copper in thin-walled niobium matrix.
etch: 30 lactic, 10 HNO_3, 3HF. 50X

Figure 4: A closer view of Figure 3 with heavier etching, above. Below, the Nb-Nb-40% Ti composite, etched.



Copper in thin-walled niobium matrix.
etch: 30 Lactic, 10 HNO_3, 3 HF. 75X.

0.1 mm



Niobium in Nb60%-Ti40% matrix. etch:
30 Lactic, 10 HNO_3, 3HF. 150X

0.1 mm

V. THE Nb-Sn COMPOSITE

ABSTRACT

To exploit the uniformity of our drawing technique, we proceeded to make simple Nb-Sn composites which were subsequently reacted to form thin Nb_3Sn layers on the inside of the wire. Very high J_c levels (10^6-10^7 a/cm^2) were attained in the Nb_3Sn layer. The wire was mechanically sound and could be bent or kinked without lowering J_c.

Layers of various thicknesses of Nb_3Sn were produced by varying the heat treating time of tin in niobium composite. A 1/2" rod of Nb 7 1/8" long was bored out to a 1/4" diameter. A tin rod, 0.24" in diameter was inserted into the hole and the material was swaged a few passes to obtain a piece long enough to draw. Because the tin is softer then the niobium, a small amount was extruded out of the ends of the niobium tube during the swaging.

In this experiment there was a sufficient amount of material between the ends to produce a segment with uniform Sn content. This niobium-clad tin was then drawn to 0.0135" wire. Sections taken showed it to be very uniform in cross-section, with some small deviation from perfect roundness. In the first experiment, wires and ribbons were sealed in vycor tubing. One third of an atmosphere of He was used to keep the vycor from collapsing at elevated temperatures. The samples were then heated to 975°C and held at that temperature for 10 nimutes, 20 minutes, 30 minutes, 4 hours and 30 minutes, 18 hours, and 70 hours. A limiting layer of Nb_3Sn, 4 microns in thickness, was formed in 2 hours. After this time, the tin evaporated out of the ends of the niobium tubing.

Mechanical sealing, welding, and all direct techniques failed to seal satisfactorily the tin core from running out. Finally the ends were sealed by a metal-to-vycor seal at one end of the vycor tube. Six samples were made and heat treated at 975°C for the following times: 10 minutes, 20 minutes, 30 minutes, 4 hours 30 minutes, 18 hours, and 70 hours. The samples shown in Figure 1 in a transverse section. This series shows the increase of the Nb_3Sn interface with increasing time. Quantitative metallography has been used to analyze this data, and the thickness of the Nb_3Sn layer vs. time has been plotted in Figure 2. $J_c(H)$ vs. H applied curves were made on these six samples at the Bitter Solenoids of the National Magnet Laboratory. These curves are plotted in Figure 3.

DISCUSSION

The diffusion couples under investigation gave information on the formation of Nb_3Sn at the interface. All showed a somewhat irregular layer with some porosity. The Nb_3Sn is most irregular at the tin interface. From the micrographs in Figure 1 and from direct measurement, it can be seen that the Nb_3Sn layer grows both into the tin and into the niobium. The growth of the tin into the niobium layer is much more uniform. In the samples heat treated for longer times, the Nb_3Sn layer is more uniform and the porosity is only near the inside. This may occur because of slow sintering of the porous Nb_3Sn. These diffusion couples show the rate of formation of Nb_3Sn at 975°C to be fast enough to produce a considerable amount of Nb_3Sn, and the layer appears to be continuous.

The Nb_3Sn thickness vs. time curve shows an initial linear slope and then a flattening off. This is to be expected. The flattening off results from the limiting amount of tin in the composite.

The J_c vs. H curves show a decrease with the length of heat treatment except for the 18 hour sample. This may be due to porosity in the thicker Nb_3Sn layer. Long time high temperature heat treatments have been shown to decrease the critical current density by other workers(1,2). This has been attributed to the sublimation of tin from the Nb_3Sn lattice(3).

Certainly the critical current densities achieved for the 10 minute heat treatment bespeak sound material, although the Nb_3Sn layer is extremely thin. One drawing sequence executed on this composite, if successful, would yield, after reaction, about a 50 or 100 fold increase in Nb_3Sn

cross-section, which in turn means very high current carrying capacity in a composite which is relatively tough mechanically; even kinks did not appear to impair J_c in any specimen.

REFERENCES

1. T. B. Reed, H. C. Gatos, W. J. LaFleur, and J. H. Roddy, in Metallurgy of Advanced Electronic Materials, G. E. Brock, Ed., p. 71. (Interscience, 1963).

2. J. J. Hanak, G. D. Cody, P. R. Aron, and H. C. Hitchcock, Proc. of VIIth International Conference on Low Temperature Physics, p. 595, Toronto, 1960.

3. T. H. Courtney, G. W. Pearsall, and J. Wulff, Trans. Met. Soc. A.I.M.E., 233, (1965).

Figure 1: Transverse sections of the Nb_3Sn/Nb composite after heat treatment.

A) 10 minutes

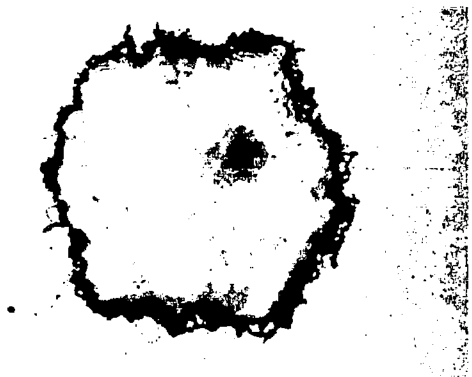
B) 20 minutes

C) 30 minutes

D) 4 Hours 30 minutes

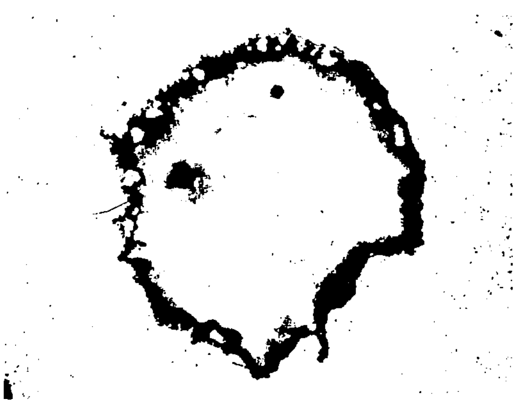
E) 18 hours

F) 70 hours

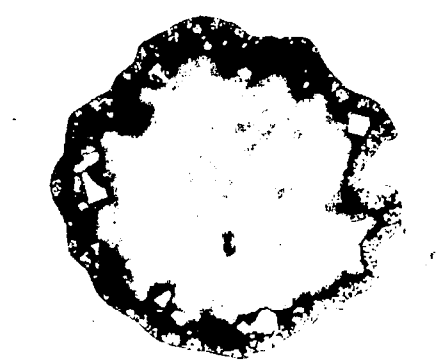


A

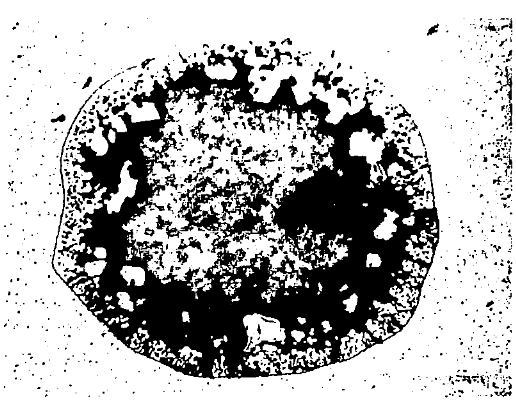
B



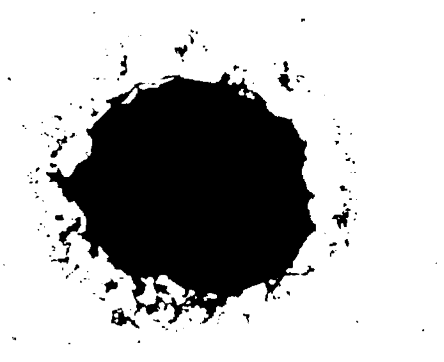
C



D



E



F

40 μ

Figure 2: Thickness of the Nb_3Sn layer as a function of the heat treating time.

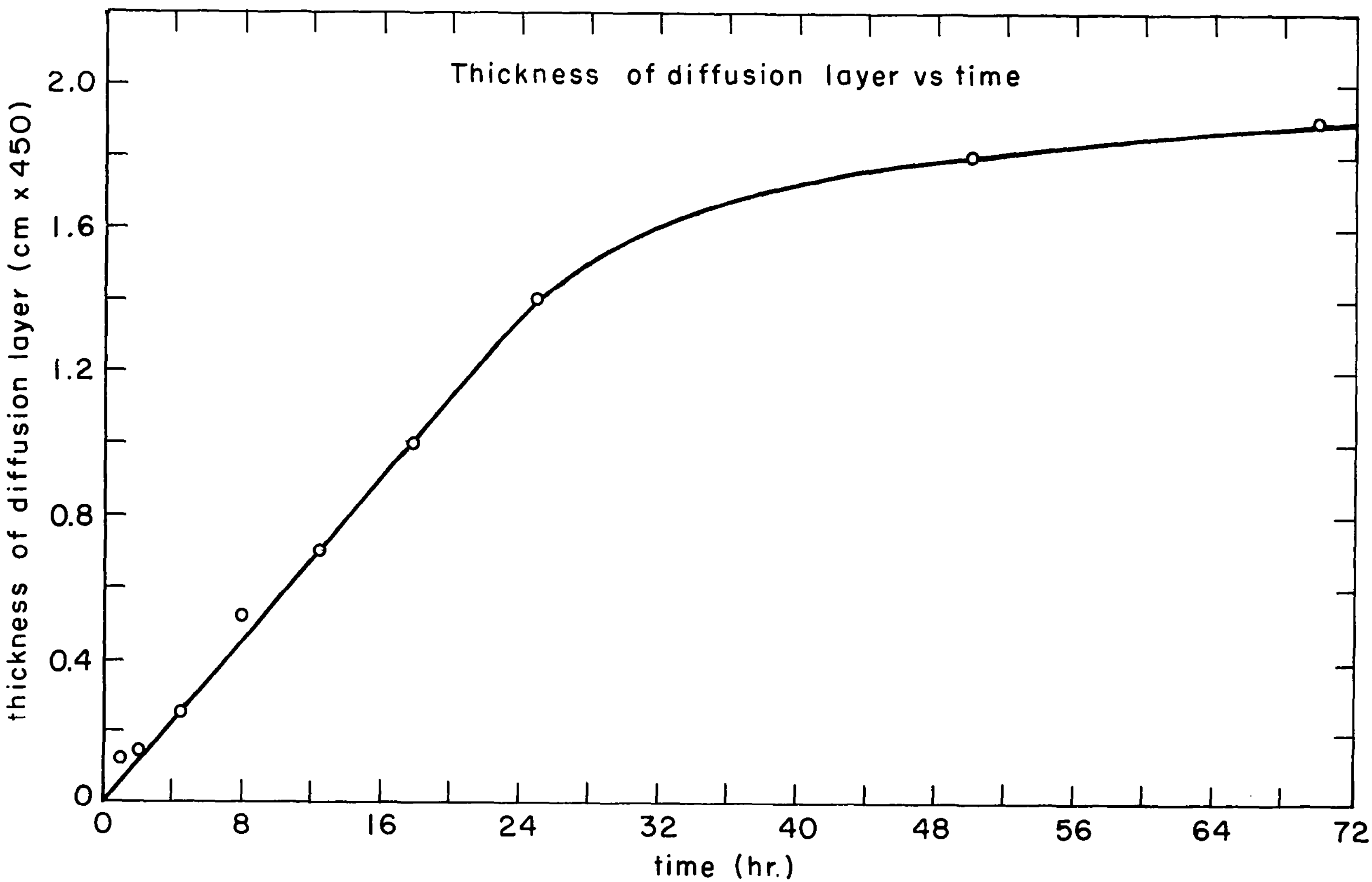
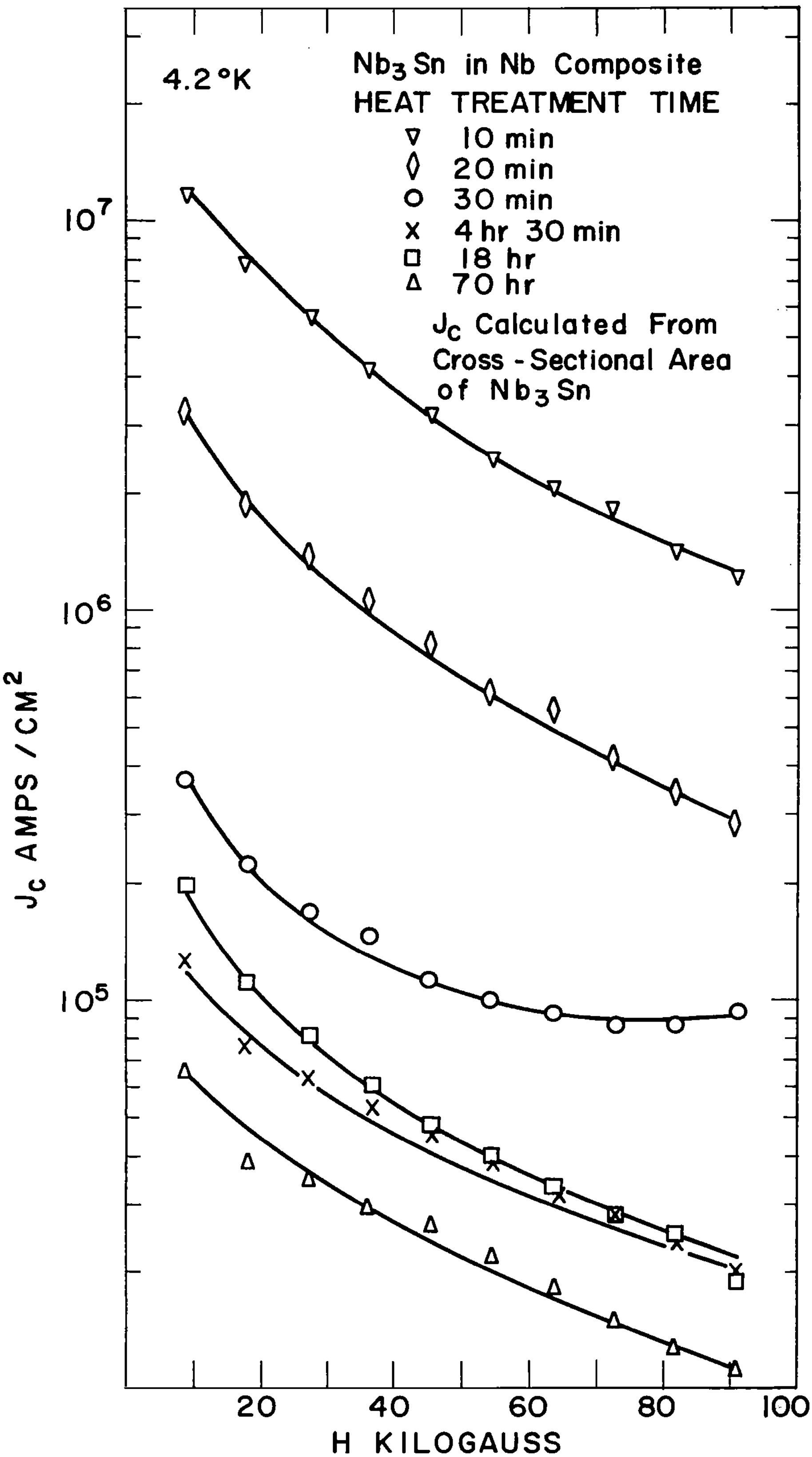

Thickness of diffusion layer vs time
thickness of diffusion layer (cm x 450)
2.0
1.6
1.2
0.8
0.4
0
0
8
16
24
32
40
48
56
64
72
time (hr.)

Figure 3: Critical current density as a function of the transverse applied magnetic field for the six samples in Figure 1. The cross-section of the Nb_3Sn layer is used to calculate the current density.



4.2°K
Nb_3Sn in Nb Composite
HEAT TREATMENT TIME
10 min
20 min
30 min
4 hr 30 min
18 hr
70 hr
J_c Calculated From Cross-Sectional Area of Nb_3Sn
10^7
10^6
10^5
J_c AMPS / CM^2
20
40
60
80
100
H KILOGAUSS

VI. SUMMARY

In an effort to understand the properties of the Nb-Th alloy, we have fabricated a series of composites and measured their properties. Several results have come of this work. First, we have shown that proximity effects occur even at large (more than 5000 A.U.) scales, and that fine multiphase structures must therefore be regarded as coherent, in a superconducting sense. Second, due to the coherence and the size effect in Type II materials, the matrix properties are very important to Type II composites, and it is doubtful that critical field enhancement can be achieved if the matrix is a nonsuperconductor. Third, the fabri ation technique developed has great promise for the low cost production of strong, flexible, high current Nb_3Sn magnet wire. Certainly the technique deserves to be developed further. Also, different composites should be fabricated for the sake of exploration of the size and proximity effect in Type II materials.

FINAL DISTRIBUTION LIST

Contract NAS3-2590

Addressee		Number of Copies
1.	NASA-Lewis Research Center 21000 Brookpark Road Cleveland, Ohio 44135 Attention: Spacecraft Technology Division	
	Albert E. Anglin	2
	James C. Laurence	2
	J. Howard Childs	2
	D. Lockwood	1
	T. Riley	1
2.	NASA-Lewis Research Center Electric Propulsion Laboratory 21000 Brookpark Road Cleveland, Ohio 44135 Attention: W. E. Moeckel	1
	E. E. Callaghan	1
3.	NASA-Lewis Research Center 21000 Brookpark Road Cleveland, Ohio 44135 Attention: Spacecraft Technology Procurement Section	1
4.	NASA-Lewis Research Center Technology Utilization Office 21000 Brookpark Road Cleveland, Ohio 44135 Attention: John Weber	1
5.	NASA-Lewis Research Center 21000 Brookpark Road Cleveland, Ohio 44135 Attention: Library	2
6.	NASA Headquarters FOB - 10B 600 Independence Ave., S.W. Washington, D. C. 20546 Attention: RNT/James Lazar	1
7.	Aeronautical Systems Division Wright-Patterson Air Force Base, Ohio Attention: ASRTCE/Harold K. Trinkle	1

	Addressee	Number of Copies
8.	Aeronautical Systems Division Wright-Patterson Air Force Base, Ohio Attention: AFAPL (APIE)/Robert Supp	1
9.	Aeronautical Systems Division Directorate of Materials and Processes Wright-Patterson Air Force Base, Ohio	1
10.	NASA-Langley Research Center Langley Station Hampton, Virginia 23365 Attention: Library	1
11.	National Magnet Laboratory M. I. T. Cambridge, Massachusetts 02139	1
12.	Metallurgy Department M.I.T. Cambridge, Massachusetts 02139 Attention: Prof. John Wulff	1
13.	Oak Ridge National Laboratory Oak Ridge, Tennessee Attention: W. F. Gauster	1
14.	National Bureau of Standards Washington, D. C. 20013 Attention: Dr. Richard Kipshot	1
15.	National Research Corporation 70 Memorial Drive Cambridge, Massachusetts 02142 Attention: Technical Information Center	1
16.	Materials Research Corporation Orangeburg, New York 10962 Attention: Vernon E. Adler	1
17.	Westinghouse Astronuclear Laboratories Electric Propulsion Laboratory Pittsburgh, Pennsylvania 15234 Attention: Mr. H. W. Szymanowski	1

Addressee	Number of Copies
18. Space Technology Laboratories 8433 Fallbrook Canoga Park, California Attention: Library	1
19. Jet Propulsion Laboratory 4800 Oak Grove Drive Pasadena, California 91102 Attention: Mr. John Paulson	1
20. Aerospace Corporation P.O. Box 95085 Los Angeles, California 90045 Attention: Library Technical Documents Group	1
21. General Electric Company Advanced Technology Laboratories One River Road Schenectady, New York 12305 Attention: R. W. Hardt	1
22. Linde Company Division of Union Carbide Corporation 270 Park Avenue New York, New York 10017 Attention: N. B. Broune	1
23. NASA-Marshall Space Flight Center Huntsville, Alabama 35812 Attention: Mr. Eugene W. Urban	2
24. Jet Propulsion Laboratories Physics Section Pasadena, California Attention: Dr. Daniel D. Ellerman	1
25. Dr. A. Septeir Faculte Des Sciences Institute D'Electronigue Orsay - Seine Et Oise, France	1
26. NASA-Lewis Research Center 21000 Brookpark Road Cleveland, Ohio 44135 Attention: Report Control Office	1

Addressee	Number of Copies
27. NASA Scientific and Technical Information Facility P.O. Box 33 College Park, Maryland 20740 Attention: NASA Representative/RQT-2448 *Plus a Reproducible	6*
28. U. S. Atomic Energy Commission Washington, D. C. 20545 Attention: William C. Gough	1
29. AFWL Kirtland Air Force Base, New Mexico Attention: WLPC/Capt. C. F. Ellis	1